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Effect of Al doping on structural and dielectric properties of PLZT ceramics

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Polycrystalline samples of Al modified lead lanthanum zirconate titanate [PLZT] with Zr = 55% and Ti = 45%, have been synthesized by a high-temperature solid-state reaction technique. X-ray diffraction analysis of the compounds suggests the formation of a single-phase compound with tetragonal structure. Dielectric studies of the compounds as a function of temperature (from 30 to 350°C) at frequency (1, 10 and 100 kHz) show that the compounds undergo a phase transition of diffuse type.The transition temperature shifts towards higher side with increase in frequency a typical characteristic of a relaxor material. Diffusivity (γ) study of phase transition of these compounds provided its value between 1 and 2, indicating the variation of degree of disordering in the system. Measurement of dc resistivity (ρ) as a function of temperature (Room temperature, RT to 350°C) at a constant biasing field suggests the compounds have negative temperature coefficient of resistance (NTCR).

1. Introduction

Lead zirconate titanate (PZT) solid solutions of the ABO_3 perovskite type structure (where A-sites are occupied by Pb^{2+} ions and B-site by Zr^{4+} and Ti^{4+} ions) show excellent piezoelectric properties. Near morphotropic phase boundary (MPB) lead zirconate titanate $Pb(ZrTi)O_3$ (PZT) is a binary solid-solution of $PbTiO_3$ ferroelectric and antiferroelectric $PbZrO_3$ [1]. Variation in chemical compositions (Zr/Ti ratio) or thermal treatment in PZT leads to a drastic change in physical properties. Several [2, 3] investigators have studied the properties of PZT or modified PZT ceramics, fabricated from high–temperature solid-state reacted powders. It has been observed that the properties of these ceramics are very sensitive to the composition fluctuation near the MPB, sintering temperature and dopant concentration. In order to achieve a high degree of molecular mixing, chemical homogeneity, control of stiochiometry, low calcination and sintering temperature, various chemical methods [4, 5] have been used for the synthesis of these compounds. But processing of PZT ceramics by a solid-solution mixing process has attracted great interest because of its inherent advantages in achieving the aforesaid properties due to its low cost in large-scale production for industrial applications. Adding oxide groups into PZT can further modify PZT; some of the oxide group additives act as ‘softeners’ and others as “hardeners”. Softeners (donors) reduce the coercive field strength, elastic modulus and aging effects and increase the permittivity and dielectric and mechanical losses. Doping of hardeners (acceptors) exhibits high p-type conductivity, reduces dielectric constant, and increase frequency constant, mechanical quality factors and aging effects. PZT are doped with acceptors ions such as K^+, Na^+ (at A-site) and Fe^{3+}, Al^{3+}, Mn^{3+} (at B-site) creating oxygen vacancies in the lattice [6,7] are known as hard PZT. On the other hand, PZT are doped with donor ions such as La^{3+} (at A-site) and Nb^{5+}, Sb^{3+} (at B-site) leading to the creation of A-site vacancies in the lattice are known as soft PZT. It is known that lanthanum oxide is effective largely because of (1) its ability to reduce the distortion (anisotropy) of the oxygen octahedral (ABO_3) unit cell thereby reducing light scattering resulting from

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the multiple refraction of light at the boundaries of the randomly oriented grains, (2) its high solubility in the PLZT perovskite structure, thus producing an extensive series of homogeneous, solid solution compositions which are free of any second phases that scatter light and (3) its ability to produce a significant number of lattice vacancies resulting in the enhancement of the densification process, control of the grain growth behavior and the promotion of a highly uniform microstructure [8]. With the growing interest in developing new materials for device applications, a large number of ferroelectric oxides have been studied in a wide range/variety of compositions and stable structures, in the form of single crystal, thin film and/or ceramics. PLZT are widely used in lighter shutters, coherent modulators, color filters, segmented displays, linear gate arrays and image storage devices [8].

PLZT is a ferroelectric ceramic formed by doping La^{3+} ions on the A-site of lead zirconate titanate. In this formula La^{3+} ions goes to the A-site and vacancies are created on the B-site to maintain charge balance. The main ferroelectric properties such as Curie temperature, spontaneous polarization, dielectric constant of PZT have been modified by single and/or double doping at A-and/or B-sites to suit for device fabrication [9–13]. By a suitable substitution at Pb/La site and Zr/Ti site in different ratio, a large number of charge neutral or charge deficient single/mixed compounds can be prepared. The preovskite compounds are normally prepared satisfying the following conditions: (a) tolerance factor and (2) charge neutrality. For ideal perovskites the tolerance factor, t should be 1. For distorted perovskite this value may be less than or equal to one. $Pb_{0.92}(La_{1-z}Alz)_{0.08}(Zr_{0.55}Ti_{0.45})_{0.98}O_3$ series has the tolerance factor $t = 0.81$. The tolerance factor and charge neutrality of the compounds suggest that the substitution of of Al^{3+} ion at La^{3+} site has distorted the cubic unit cell to the tetragonal unit cell. In view of the dramatic change in physical properties of PZT on double doping, we have carried out systematic study of structural and electrical properties of Al modified PLZT ceramics.

2. Experimental procedure

Polycrystalline samples of Al modified (PLAZT) ceramics with general formula $Pb_{0.92}(La_{1-z}Alz)_{0.08}$ $(Zr_{0.55}Ti_{0.45})_{0.98}O_3$ ($z = 0.0$, 0.3, 0.5, and 0.7%) were synthesized from high purity oxides: PbO (99.9% M/S Aldrich chemicals USA), TiO_2 (99.9% M/S s.d.fine-Chem Ltd.), La_2O_3 (99.99% M/S Indian Rare-Earth Ltd), Al_2O_3 (99.999%, M/S Aldrich Chemicals USA) and ZrO_2 (99.99%M/S Aldrich chemical, USA) using a high-temperature solid-state reaction technique in an air atmosphere. The raw materials of the required compositions were mixed in a ball milling for 24 h in the presence of methanol using zirconia balls. The calcination was done at a temperature 800°C for 2 h. Before compaction, the calcined lump was ground and granulated to convert it to a uniform free flowing aggregate by addition of small quantity of PVA as binder. The fine powders so obtained was pressed into discs (pellets) of 10 mm diameter and 1 mm thickness under a pressure of 7×10^6 kgm^{-2} using a hydraulic press. The pellets were sintered in air atmosphere at 1200°C for 2 h in presence of $PbZrO_3$ powder, to prevent PbO loss during the high temperature sintering. Sintered pellets were electroded by high-purity silver particle paste, and fired at 150°C, before using for any electrical measurements.

Powder X-ray diffraction was recorded by a X-ray powder (Philips) diffractometer using Cuk_α radiation ($\lambda = 1.5418$ Å) in wide range of Bragg angles ($20° \leq 2\theta \leq 60°$) at a scanning rate of 2°/min.

The dielectric permittivity (ε) and loss tangent ($\tan\delta$) of the samples were measured as a function of frequency at different temperature (room temperature to 360°C) using a HP4623B LCR meter. A three-terminal sample holder,

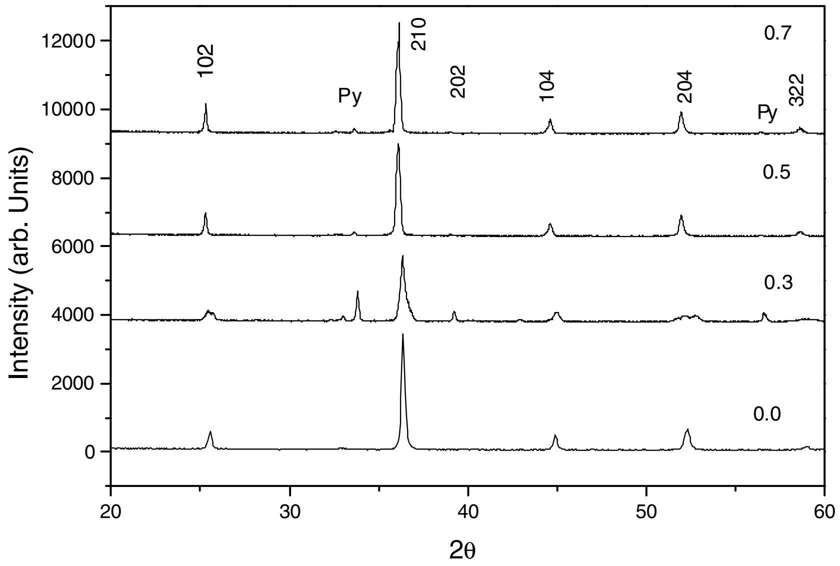

Figure 1 X-ray diffractogram of PLAZT.

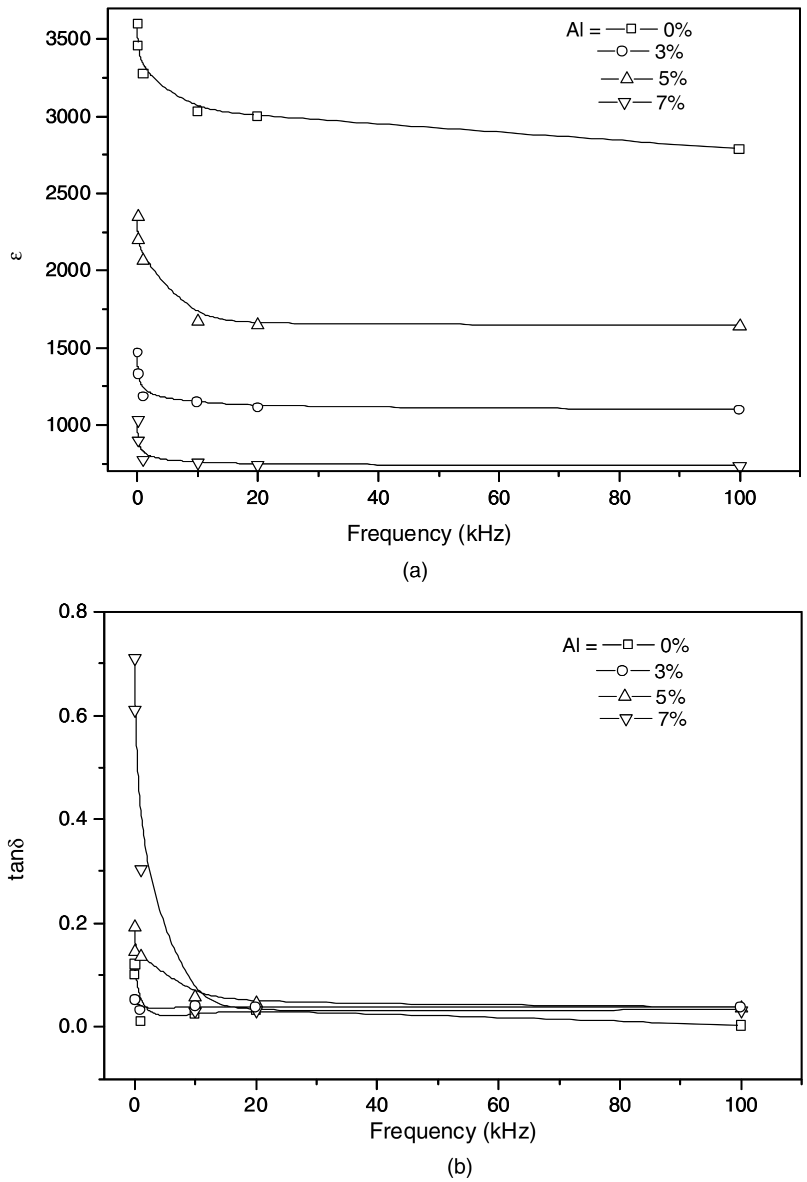

Figure 2 (a) Variation of dielectric permittivity (ε) of PLAZT as a function of frequency at room temperature. (b) Variation of (tan δ) of PLAZT as a function of frequency at room temperature.

designed and fabricated in our laboratory, was used for these measurements to compensate any stray capacitance. DC electrical resistivity was measured as a function of temperature at voltage of 10 V using Keithley 617 programmable electrometer and laboratory fabricated three-terminal sample holder and heating system. The temperature was recorded using a chromel-alumel thermocouple.

3. Results and discussion

The XRD patterns of the PLAZT ceramics show (Fig. 1) sharp and single diffraction peaks, which indicate a better homogeneity and crystallization of the samples. All the reflection peaks were indexed and lattice parameters of PLAZT were calculated using a computer program based on a least squares refinement method (Powdin). It is observed that pure and Al^{3+} modified PLZT belongs to tetragonal structure. Our observation of tetragonal system is very much consistent with the well-established phase diagram of PLZT [14]. A good agreement between calculated and observed d-values of all diffraction lines (Reflection) of PLAZT X-ray pattern, with the different compositions suggests that there is no change in the basic crystal structure of PLAZT. However, some changes in the intensity of a few reflections have been observed which may be due to (i) variation of particle size and (ii) the presence of Al^{3+} in different z values. As the concentration of Al increases the intensity of the diffraction peaks increases. As Al possess lower atomic number than La, contribution to the intense peak due to Pb increases as the concentration of La decreases with increase in Al content. This and other experimental observations (eg. dielectric and electrical) suggest that Al^{+3} (even with low atomic number) has gone to the La^{+3} site and has significant effect on the

TABLE I Comparison of lattice parameters of PLAZT samples

Lattice parameters in (Å)	Composition Al%			
	0%	3%	5%	7%
a = b	4.0487	3.8928	3.9615	3.9666
c	4.1937	4.0680	4.0725	4.0619
c/a	1.036	1.045	1.028	1.024
Volume (Å)	68.74	61.64	63.91	63.90
Measured Density(gm/cc)	7.45	7.70	7.62	7.69

TABLE II Dielectric parameters of PLAZT samples

Physical Parameters	Compositions Al%			
	0%	3%	5%	7%
$\varepsilon_{\max}$ at1 kHz	4715	4611	12152	12443
$\varepsilon_{\max}$ at10 kHz	4451	3677	9903	11666
$\varepsilon_{\max}$ at100 kHz	3955	3618	6733	11099
E_a at 1 kHz	0.89	0.13	0.33	0.13
at 10 kHz	0.88	0.25	0.35	0.20
at 100 kHz	0.80	0.23	0.50	0.18
Diffusivity (γ)				
at 1 kHz	1.82	1.86	1.88	1.90
at 10 kHz	1.83	1.86	1.89	1.91
at 100 kHz	1.85	1.88	1.90	1.93
ρ_{dc}(RT) ($\times 10^{11}\,\Omega$m)	13.8	14.6	16	16.8
T_c at 1 kHz	440	483	514	590
at 10 kHz	445	487	520	594
at 100 kHz	463	495	529	599

physical properties of PLZT. The c/a ratio decreases with the substitution of Al^{3+} ions in PLZT structure. The density measured by the geometry of the samples, lattice parameters and unit volume cell of the samples are given in Table I.

Fig. 2a and b shows the variation of dielectric permittivity (ε) and loss tangent (tanδ) of all the samples with frequency at room temperature. It may be noted that in all samples, there is an increase in the dielectric constant with decreasing frequency, which is a typical characteristic of normal dielectric [11]. The decrease in dielectric constant arises from the fact that polarization does not occurs instantaneously with the application of the electric field because of inertia. The delay in response towards the impressed alternating electric field leads to loss and decline in dielectric constant. At low frequencies, all the polarizations contribute. As frequency is increased, those with large relaxation times cease to respond and hence the decrease in dielectric constant. The loss (tanδ) decreases with increasing frequency. The decreases in of tan with increasing frequency may be described on the basis of Koop's phenomenological model [12]. It is observed that at higher frequency, these parameters became almost frequency independent [13].

Fig. 3a–c show the variation of dielectric permittivity (ε) with temperature at different (1, 10 and 100 kHz) frequency. ε increases gradually to its maximum value ($\varepsilon_{\max}$) with increase of temperature up to transition temperature (T_c) and then decreases smoothly for all the compositions. It is clear from fig that materials undergo a phase transition from the ferroelectric to the paraelectric phase on heating. However the dielectric peak is broadened around the maximum value of ε, which indicates the existence of a diffuse phase transition in PLAZT. Here the transition temperature of PLAZT ceramics increases with increasing Al concentration. The broadening in phase transition is attributed due to the structural disorder and compositional fluctuation present [14] in the arrangement of cation at A-site and B-site with lattice vacancies, leading to a microscopic heterogeneity in the composition, and thus results in the distribution of different local Curie points. There is obvious dielectric frequency dispersion as shown in Fig. 3a–c. As the frequency increases, the transition temperature shifts towards the higher temperature side.This is a typical characteristic of a relaxor material [13].

The quantitative assessment of the diffuseness (γ) of the broadened peaks in the paraelectric phase was evaluated using the expression $\ln(1/\varepsilon - 1/\varepsilon_{\max})$ vs $(T - T_c)^{\gamma}$ [15]. The plot of $\ln(1/\varepsilon - 1/\varepsilon_{\max})$ vs $\ln(T - T_c)$ for all compositions was extracted from the plot by fitting a straight line equation (Fig. 4). The value of γ calculated from Fig. 4 ranging from 1(normal Curie Weiss behavior) to 2 (completely disordered), shows the diffuse phase transition in the materials. The linear increases in γ with an increase in frequency suggest that the broadening effect on the phase transition is more pronounced at higher frequency.

The a.c electrical conductivity for all the samples was calculated from the conductivity relation $\sigma = \omega\varepsilon\varepsilon_0 \tan\delta$ where ε_0 is the vacuum dielectric permittivity and ω is the angular frequency [16]. Further the activation energy (E_a) was evaluated from the lnσ_{ac} versus 10^3/T curve (Fig. 5) and using the conductivity relation $\sigma = \sigma_0 e^{Ea/kBT}$ (where k_B is the Boltzmann constant). The values of E_a for all compositions at different frequency are given in Table II. The value of activation energy in the paraelectric phase is found to be very low. The low value of the activation energy has been observed in many Pb-based ferroelectric complex compounds [17]. This may be due to ionic solids having a limited number of mobile ions being trapped in relatively stable potential wells during their motion through the solid. Due to a rise in temperature the donor cations are taking a major part in the conduction process. The donors have created a level (i.e, band-donor level), which is much nearer to the conduction band. Therefore, only a small amount of energy is required to activate the donors. In addition to this, a slight change in stiochiometry in multi–metal complex oxides causes the creation of large number of donors or acceptors, which creates donor or acceptors like states in the vicinity of conduction or valance bands. These donors or acceptors may also be activated with small energy [18].

The temperature dependence of resistivity is shown in Fig. 6. It has been found that the dc resistivity decreases with increase in temperature because of the addition of thermal energy. The addition of Al enhances the resistivity characteristic. This variation also shows that the

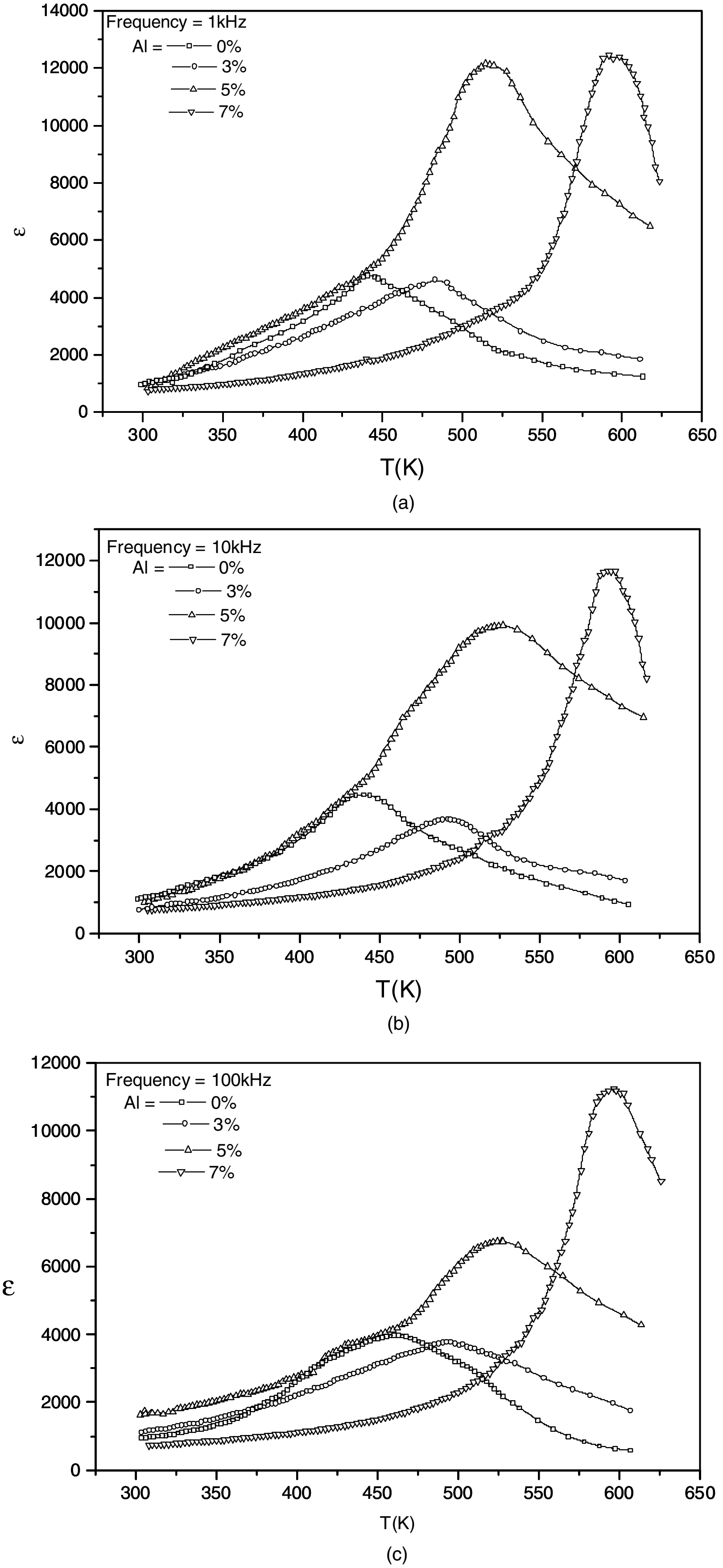

Figure 3 (a–c) Variation of (ε) of PLAZT as a function of temperature at 1 kHz, 10 kHz and 100 kHz.

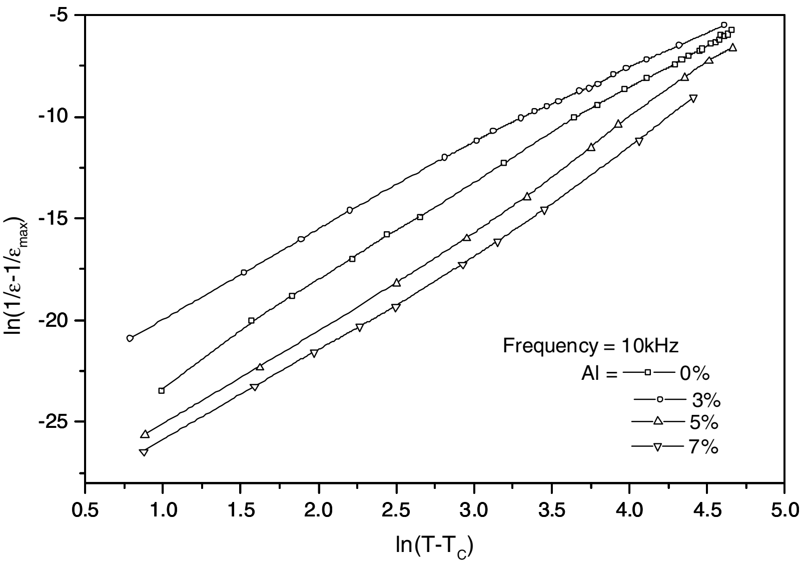

Figure 4 Variation of $\ln(1/\varepsilon - 1/\varepsilon_{\max})$ vs $\ln(T - T_C)$ in the paraelectric region at 10 kHz.

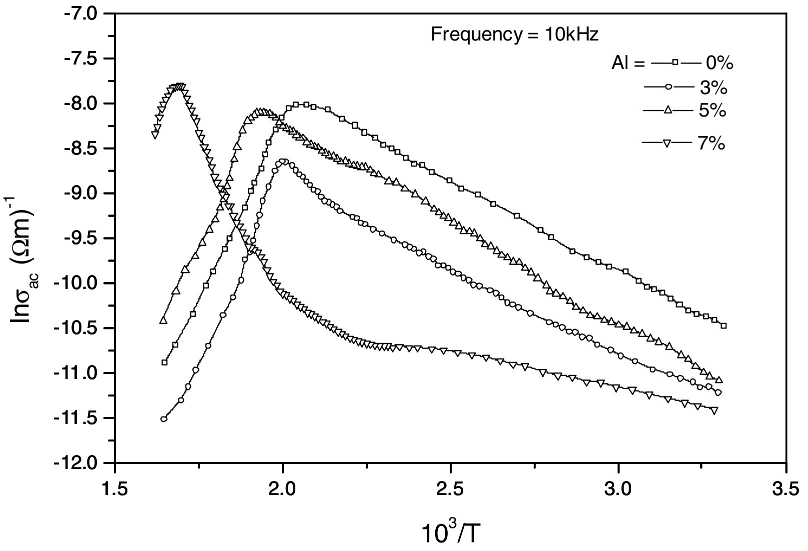

Figure 5 Variation of a.c conductivity ($\ln\sigma$) as a function of inverse of absolute temperature ($1/T$) of PLAZT at 10 kHz.

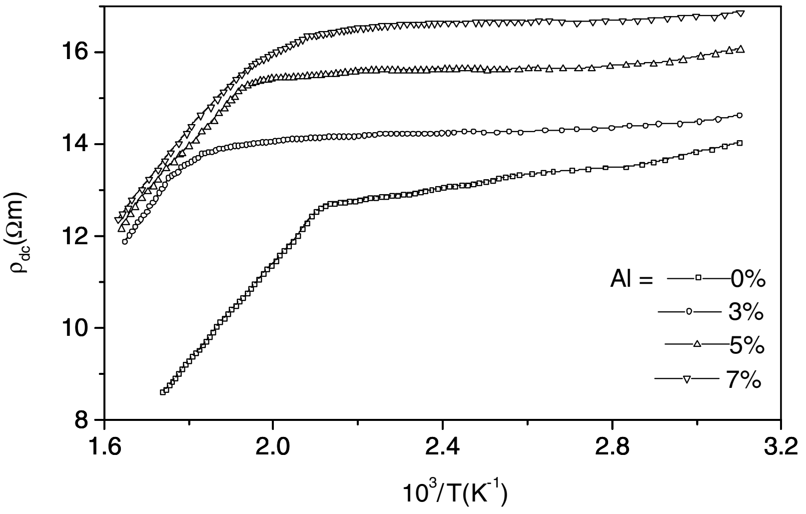

Figure 6 Variation of dc resistivity $\ln \rho$ vs $10^3/T$ of PLAZT at 10 V/cm.

compound has negative temperature coefficient resistance (NTCR) [19, 20]. The nature of variation of specific resistivity with temperature of all the compounds containing various amounts of (Al) was found to be very similar except in low—temperature region. In this region, the value of resistivity increases with increase in Al^{+3} ion concentrations; this is because of electron–hole compensation [21, 22].

4. Conclusion

PLAZT ceramics exhibit tetragonal crystal structure at room temperature exhibiting better homogeneity and formation of pure perovskite phase. Al doping in PLZT exhibits shift in transition temperature, increase in diffusivity of the FE-PE phase transition and increment in dielectric constant, resistivity of the materials diffuse phase transition and increment in dielectric constant. The compound also exhibits NTCR characteristics and may be useful in the fabrication of electronic/electrical devices.

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